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## **PRODUCTION OF SHAPED PARTS OF NITINOL ALLOYS BY SOLID-STATE SINTERING**

BY DAVID M. GOLDSTEIN

RESEARCH AND TECHNOLOGY DEPARTMENT

15 OCTOBER 1984

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  A solid state sintering process has been successfully adapted to consolidating NITINOL alloy powders. NITINOL alloys are noted for their shape memory properties. The sintering process is performed at atmospheric pressure upon powders contained in an evacuated glass container.	Processing parameters are reported. Tubes and tubular tees were made as well as solid round bars. Round bar stock was extruded and swaged. Excellent shape memory properties were obtained.	

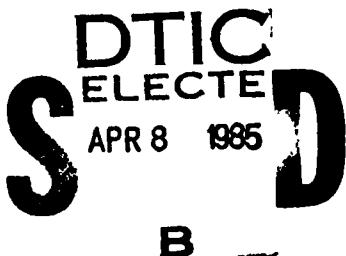
## FOREWORD

This report presents the results of an Independent Exploratory Development (IED) Program conducted by the Naval Surface Weapons Center. Some portions of the Program were performed by the Specialty Steel Division of the Cyclops Corporation. This study demonstrated that a low-cost, solid-state process developed for tool steel manufacture could be successfully adapted to the manufacture of NITINOL (TiNi) alloys. This publication presents the state of the art of producing bulk metal and near net shape products from pre-alloyed NITINOL powders. The assistance of Mr. Robert Gasior and Cyclops Corporation is gratefully acknowledged.

Company and trade names are used in this report for technical information only.

Approved by:

J. R. Dixon  
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Materials Division



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CHAPTER 1

INTRODUCTION

NITINOL is an alloy of nickel and titanium which exhibits a shape memory effect. The term "shape memory effect" (SME) is used to describe the ability of certain alloys which, if deformed at a low temperature, will recover their prior shape when heated.

The first shape memory alloy with engineering properties was invented by Buehler and Wiley. Their patent for the alloy was filed in 1961 and granted in 1965. Upon the discovery of its unique properties, Buehler and Wiley designated the alloy as 55 NITINOL, to connote its composition and place of origin, i.e., 55 weight percent Nickel, remainder Titanium. NOL was derived from the Naval Ordnance Laboratory, which is now the Naval Surface Weapons Center.

COUPLINGS, BACKGROUND

A major early application based on NITINOL was the Cryofit® coupling designed by the Raychem Corporation, Menlo Park, California, in 1969. This excellent coupling provided a pressure tight end-to-end connection between two tubes. Currently in wide use, it operates by contracting from its expanded diameter upon being warmed to room temperature. The term "heat recoverable coupling" (HRC) came into use at shipyards, with the use of the couplings for heavy wall piping for working pressures of 6000 psi. Expanded HRCs are stored in liquid nitrogen until they are used. Heating the installed coupling is accomplished by ambient air. The extensive developmental and test work initiated by the Naval Sea Systems Command and the Raychem Corporation in 1973 ultimately led to the use of the Cryofit HRCs in shipboard piping systems. Lockheed, also in 1973, tested a 4-inch diameter coupling for the Navy.<sup>1</sup> In 1975, the Electric Boat Division of General Dynamics recommended that a program be conducted to qualify the couplings for possible use with submarines.<sup>2</sup> Raychem presented a paper in 1975 to the Sixth Submarine Hydraulics Conference<sup>3</sup> reporting on the use of the Cryofit System by Vickers Shipbuilding Limited in British nuclear submarines. Ingalls Shipbuilding Division reported on the successful introduction of HRCs into new naval construction in 1979.<sup>4</sup> Based on a 1981 study at Pearl Harbor Naval Shipyard, LCDR Baskerville, USN, projected the potential usage of HRCs at the eight naval shipyards at 35,000 couplings per year.<sup>5</sup> On the supply side, Raychem currently offers a standard size range of Cryofit HRCs for pipe sizes from 1/8 inch to 1-1/2 inch. Caskey and Embry<sup>4</sup> recognized the advantages that would accrue if shapes were to become available, in addition to couplings. A report within the Naval Sea Systems Command<sup>6</sup> subsequently reviewed the advantages of the development of shaped fittings, such as tees, ells, etc.

## SOLID-STATE SINTERING

Historically, NITINOL alloys have been produced almost exclusively by melting processes. These included arc, electron beam, and induction methods, frequently with second and even third re-melts. These techniques are required by the nature of the alloy constituents, by the very narrow range of chemistry allowed, and by the criticality of compositional homogeneity. The correlation of charge, or analysis, chemistry with transition temperatures (SME recovery temperatures) for NITINOL alloys has, in general, been inexact. The scatter of the data is visible in Figure 1. It is, however, to be recognized that heat treatments and the different methods used to measure transition temperatures introduced their own contribution to the scatter.

In addition to the compositional (and, therefore, transition temperature) variation from the melting process, there is an additional limitation in the casting of NITINOL. This is due to the tendency of NITINOL, like other high titanium content alloys, to react with the mold materials. Shape production, therefore, tends to be limited to very high value parts, due to mold costs.

Preparation of bulk metal by the solid-state sintering of pre-alloyed powders is a means of avoiding these limitations.<sup>7,8,9</sup> The Naval Surface Weapons Center and others have engaged in sporadic efforts to consolidate elemental nickel and titanium powders by cold isostatic pressing and subsequent sintering. Shape response of these materials was pronounced, but inferior to that of a cast and wrought product. Pre-alloyed powders processed in the same way tended to crack upon sintering of the cold pressed compact.

These difficulties suggested that hot isostatic pressing of pre-alloyed powders would be a more assured route of achieving bulk metal with the desired characteristics. Special Metals Corporation (SMC), New Hartford, New York, and Ann Arbor, Michigan was invited to produce several experimental powder lots to test this thesis. This resulted in the production of sintered and wrought NITINOL wire with performance matching that of the cast and wrought product.<sup>10</sup> Their successful atomization of 50-pound melts and subsequent consolidation of the powders was a significant technical accomplishment. SMC is now a producer of NITINOL alloys. Although the hot isostatic pressing technique which was used produced a high-quality product, it remains as a relatively high cost method of consolidating powders to near net shape. It should be kept in mind, however, that the method itself produces high-quality bulk material, and is used for example, for highly stressed parts such as superalloy turbine wheel discs. This will be of interest and will be discussed subsequently, when the objective of the hot isostatic pressing operation is increased densification, rather than the initial sintering.

In 1981 the Specialty Steel Division (since renamed "Cytemp") of Cyclops Corporation publicized a procedure which could substitute for hot isostatic pressing. Their process, identified as a Consolidation by Atmospheric Pressure (CAP<sup>11</sup>), entailed the use of glass molds and standard air-atmosphere furnaces. With such simple equipment the process can, and does, compete in the marketplace of modestly priced tool steels. These economics also looked attractive when applied to the substantially higher priced NITINOL alloys. It remained to be established, however, that the CAP process was applicable to NITINOL alloys.

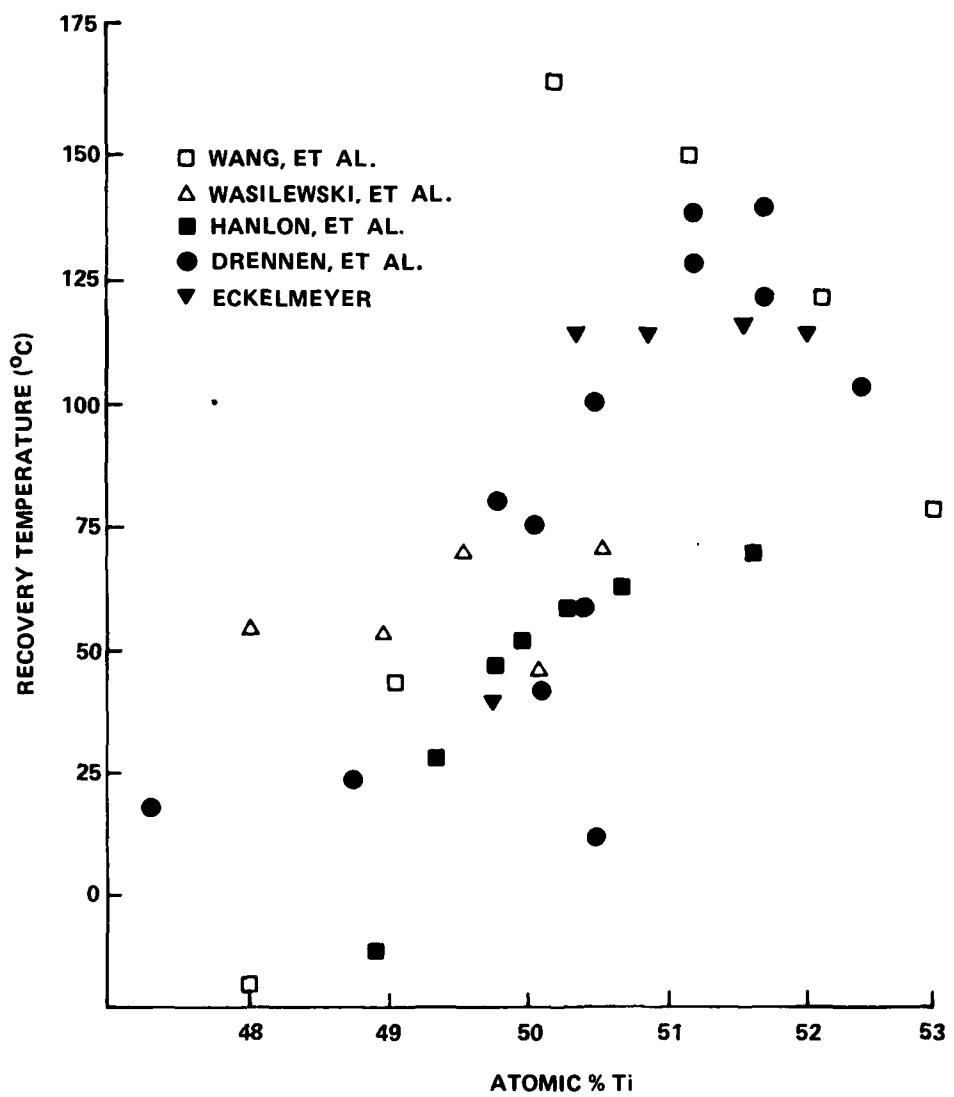


FIGURE 1. PREVIOUSLY REPORTED DATA ON THE EFFECT OF COMPOSITION ON THE RECOVERY TEMPERATURE OF NiTi ALLOYS (REFERENCE 7)

SHAPED PARTS

Directly and through its contractors the U.S. Navy is a major user of commercially manufactured HRCs. The Grumman-manufactured F-14 (TOMCAT) naval aircraft contains a substantial quantity of HRCs in its hydraulic systems. The newly constructed CG 76 (TICONDEROGA) and DDG 51 (BURKE) ships use HRCs. As a result of overhaul and repair (O & R) activities, every major class of naval surface ships now has HRCs aboard. The significance of pipe joining in these O & R activities (and impact of major retrofit programs, e.g., USS IOWA), were reviewed in a Navy study on ship overhaul costs.<sup>11\*</sup>

Cryofit HRCs, despite their relatively high cost, achieve their savings through their reduction of installation labor, inspection costs, and rework of damaged adjacent areas that occur in welding in restricted spaces.<sup>11</sup> Additionally, unlike welding, they may be used in repair of systems containing flammable fluids without purging the system.

HRCs were identified as a new technology for shipbuilding<sup>12</sup> in 1981, and as such fitted precisely into the guidelines of the Navy's Manufacturing Technology and Shipbuilding Technology (MT/ST) Program Plan.<sup>13</sup>

Clearly, HCRs have established their value to the piping crafts.

Given the Navy's long involvement with shape memory alloys and the HRCs based on them, the development of shaped fittings for piping systems is an evolutionary step in increasing NITINOL utility to the Navy. This report describes progress in this direction.

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\*From Reference 11, "The second largest potential for payoff in piping systems repair is in the labor costs for installing pipe sections in ships. The largest payoff itself is in reducing the time that submarines and carriers spend in overhaul while having valves overhauled. Piping and valve repair together constitute a major cost in overhaul."

CHAPTER 2  
THE CAP PROCESS FOR NITINOL

BACKGROUND

The CAP process<sup>14</sup> is one variant of many different powder metallurgy consolidation procedures. The common starting material for these procedures is usually a powder, often pre-alloyed. The advantages of powder sintering techniques include fabrication to near net shape, resulting in lowered finished part cost; improvement of selected mechanical properties; and fabrication of alloys not readily amenable to hot working. The CAP process is performed on powders which have been contained in a glass mold. The glass itself is the same borosilicate composition widely found in laboratory ware bearing the names Kimax® and Pyrex®. The CAP procedure is to fill a glass mold of the selected part shape with powders of the desired alloy composition, evacuate, and seal the mold under a high vacuum. The sealed glass envelope is then submerged in a crucible containing a refractory powder bed which will flow freely at the planned sintering temperature. The crucible is placed in any air atmosphere furnace of suitable design and heated to the selected temperature. During the course of heating, the glass softens and flows inward under the pressure exerted by the atmosphere. The free-flowing refractory bed, which surrounds the glass, provides support for it as it softens. This enables dimensional change to occur without significant shape change.

A commercial sintering cycle is typically 12 to 24 hours for glass enveloped large parts, followed by partial cooling in the furnace and then removal from the furnace. During cooling to below red-heat temperatures the glass envelope self strips from the metal. This is due to the differential of their contraction rates. The resultant metal part may be as high as 99 percent dense.

As practiced by Cyclops, CAP preforms as large as 2000 pounds have been produced. Alloy tool steels and a variety of super alloys, mostly with nickel bases, have also been consolidated by the CAP process.

Determination of whether the CAP process was applicable to NITINOL alloys began at the Naval Surface Weapons Center by using powders produced earlier by Special Metals Corp. These powders were produced from NITINOL ingots made in a consumable electrode arc furnace. This latter method of melting produces an ingot which may not be homogeneous either from side to side or bottom to top.

The SMC arc-melted ingots were re-melted in a vacuum induction furnace using a graphite crucible and atomized. While it is possible to directly induction melt and atomize the alloy by starting with elemental metals, it is less reliable than starting with the pre-alloy; this is due to the reactivity of elemental liquid titanium with graphite, which is negligible when it is buffered with nickel.

Induction melting inherently produces a homogeneous liquid melt, a desirable feature for the subsequent atomization. As the liquid metal is poured in a thin stream from a specially designed pouring cup, it is impacted by one or more jets of high pressure inert gas. The gas jets cause the liquid stream to diverge into liquid droplets, which rapidly solidify into sliver-like and globular shapes. These atomized particles range in size from as long as 5 or 6 mm (1/4 inch) to as small as spheroids less than 44  $\mu\text{m}$  ( $\sim 0.002$  inch). The powders are cooled in the inert atmosphere, emerging as bright to grey in color (depending on size), and are essentially oxide free. They are not subject to instantaneous combustion and do not appear to burn readily, allowing ready handling of the powders in air. The powders from the various melts (identified as "Heats") were the starting materials for the following technical effort.

#### EXPERIMENTAL CONDITIONS AND PROCEDURES

The following experiments delineated the conditions under which CAP processing would or would not be successful for NITINOL.

##### Powder Packing

Powder packing is a function of powder size, shape, and mesh fractions used. For -60 mesh Heat R79359 the packing factor was 50 percent; for -100 mesh Heat 81510 it was  $\sim$ 56 percent. These values are based on the density of solid NITINOL being 6.45 g/cc (0.234 lb/in<sup>3</sup>); thus these are percentages of theoretical density (TD).

##### Evaluation Procedures

Powders ( $\sim$ 60 grams) were poured into test-tube shaped containers with enlarged lower sections. These were outgassed for 1/2 hour to a pressure of 0.7  $\mu\text{m}$ .

##### CAP Processing

An evacuated and sealed glass envelope with  $\sim$ 60 grams of -100 mesh Heat 81510 was submerged in a plumbago (clay graphite) crucible containing Dixon 1101 flake graphite at 25°C. The crucible was heated and held at 950°C to 975°C for 12 hours. It was furnace cooled overnight to 600°C. The specimen was removed from the crucible, causing about 95 percent of the glass envelope to undergo self stripping. The specimen was integral and had increased to  $\sim$ 62 percent of TD. This demonstrated that NITINOL could achieve sintering under CAP processing.

Subsequently it was shown that sintering at 1110°C for 20 hours could produce 65 percent of TD for -60 +100 mesh powders from Heat 81512, and also for -100 mesh powders of Heat 81510 to which 5 percent by weight of -80 mesh nickel powder had been added.

Raising the sintering temperature still further, to 1165°C, had a substantial effect in that it produced sintering to 91.5 percent of TD in as little as 4 hours. This followed an 1100°C conditioning treatment for 20 hours. The powder used was -100 mesh Heat 81510. The 91.5 percent of TD was a successful culmination of sintering tests, since it enabled ingots to be subsequently hot worked in air.

While the soak at 1165°C for 4 hours increased the density achievable with -100 mesh powder, it had no comparable effect on previously CAP processed Heat 81512, -60 +100 mesh powder which had been sintered to 65 percent of TD at 1110°C. Re-encapsulation and the subsequent 1165°C treatment of this small ingot (81512 powder) increased its density to only 68 percent, up 3 percent from the 65 percent of TD following the original 1110°C treatment. The results of these preliminary experiments are shown in Table 1.

The same graphite flake bed and a single plumbago crucible were reused throughout these experiments. A layer of graphite flake about 1/4 inch thick, atop the 8-inch deep bed was ashed during each experiment. This thin layer was skimmed off and discarded. This is an attractive materials utilization and reuse program, helping to maintain low operating costs. Furthermore it is a materials conservation process in that no alternative protective atmospheres are required in the furnace for CAP processing.

#### Powder Sizing

Line 5 of Table 1 suggests that the re-sintering of a -60 +100 mesh powder compact (Heat 81512) at a higher temperature did not significantly densify it further. This implies that CAP processing of virgin -60 +100 powder of itself will not satisfactorily sinter the coarser powder at 1175°C within 4 hours. This is in contrast to the excellent sintering of -100 mesh powder (Heat 81510), Line 4. In general, use of larger mesh sizes of powder improves the economics of production. It is therefore desirable to know if powder as coarse as -60 mesh NITINOL can be used in the CAP process.

To test this thesis, powder from Heat 81512, -60 +100 mesh was selected. To corroborate the results of Heat 81512, Heat 81511, -60 +100 was also used. Also evaluated was a blend of Heat 81511, -60 +100 with Heat 81510, -100 mesh. The latter blend was 1/2 by weight of each Heat, providing some filler for the interstices of the coarse fraction, but not necessarily the optimum amount. The processing cycle was 1175°C for 8 hours. The results given in Table 2 are indicative of the effect of powder size. For the blend, the densification is a function of the fractions of each mesh size present in the virgin powder.

From the data in Tables 1 and 2 it appears that CAP processing of virgin powders of -60 +100 mesh will sinter at 1175°C to a maximum of 68 percent of TD. Table 2 shows that blending with finer powders did increase the densification from ~60 to 76 percent of TD. A confirmatory test on only Heats 81510 and 81511 with both a replicated cycle of 1175°C for 8 hours and also the extended time of 24 hours was performed. From the data shown in Table 3 it can

TABLE 1. DENSITIES OF NITINOL POWDER COMPACTS AFTER CAP PROCESSING

LINE	HEAT NUMBER	POWDER SIZE, MESH*	SINTERING TEMP. °C	TIME, HRS.	RESULT % TD
1	81510	-100	950-975	12	62
2	81512	-60 +100	1110	20	65
3	81510 w/5% addition of - 80 mesh Nickel powder	-100	1110	20	65
4	81510	-100	1100 1165	20 4	91.5
5	81512**	-60 +100	1100 1165	20 4	68

\*mesh size openings:

-100 mesh = 0.006"  
-80 mesh = 0.007"  
-60 mesh = 0.010"

\*\*Portion of Previously Sintered 65% Dense Bar, Re-encapsulated.

TABLE 2. EFFECT OF POWDER SIZE ON DENSIFICATION OF NITINOL POWDERS  
(CAP PROCESSED AT 1175°C FOR 8 HOURS)

	HEAT NUMBER	MESH SIZE	% OF TD
#44	81512	-60 +100	59
#43	81511	-60 +100	63
#42	1/2 81511 1/2 81510	-60 +100 -100	76
#4	81510*	-100	91.5

\*Processed at 1100°C for 20 Hours Followed by 1165°C for 4 Hours.

TABLE 3. EFFECT OF SINTERING CYCLE AND POWDER SIZE ON DENSIFICATION OF NITINOL (CAP PROCESSING AT 1175°C FOR 8 HOURS VS 24 HOURS)

POWDER		% OF TD	
HEAT NUMBER	MESH SIZE	8-HR CYCLE AT 1175°C	24-HR CYCLE AT 1175°C
81511	-60 +100	80.2	82.3
81510	-60 +100	83.9	86.2
1/2 81511 1/2 81510	-60 +100 -100	80.5	79.8
81510	-100	92.0	92.1

be seen that a 24-hour sinter time offers only an insignificant increase in densification over an 8-hour cycle. This table also shows that mixtures of powders containing -60 mesh powder will densify to 80 to 86 percent of TD as compared to 92 percent of TD for -100 mesh powder.

#### Mechanical Processing

Three round bars, approximately 15 mm (0.6 inch) in diameter by 11 cm (4-1/2 inches) in length, were produced by CAP processing to densities 91-1/2 percent of TD or greater. This density can be hot worked in air. Figure 2A presents the first bar of the three, as CAP processed. A rod hot swaged and machined from the second bar, Figure 2B, and wire drawn from the third bar, Figure 2C, are also shown.

The three bars were made from -100 mesh Heat 81510 powders. After swaging from an 850°C furnace to a 50 percent reduction in area, the density of the second bar increased to 98 percent of TD from its original "as CAP" density of 91.5 percent TD. Wire was readily drawn from the third bar after it was hot swaged to 6 mm (0.250 inch) in diameter and then cold swaged to 3.3 mm (0.130 inch) in diameter with intermediate brief anneals at 600°C. The wire drawing was done at 25°C, using 10 percent reductions in area, without lubrication of the wire. No breakage of the wire occurred, demonstrating that the CAP process can produce a high quality of wire. The wire was reduced to 2.8 mm (0.111 inch) with intermediate anneals. This was a 28 percent reduction in area by wire drawing. Subsequently the wire was reduced to 1.5  $\mu$ m (0.062 inch) in diameter by a variety of treatments including intermediate annealing, refrigerating, swaging, and drawing. These latter were for the purpose of enhancing the shape memory response. Bend tests showed the swaged and drawn wire to perform as well as cast and wrought wire in shape recovery.

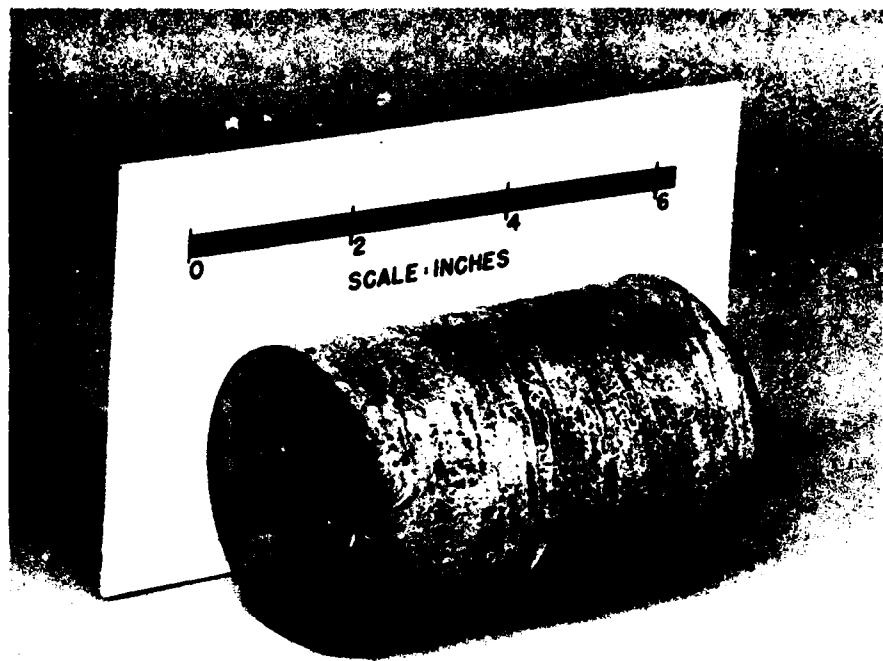
Hot extrusion of bare CAP processed ingot was unsuccessful (due to "fir tree" break-up) when done under the general conditions which are effective for cast NITINOL ingots. To demonstrate that CAP processed material would extrude it was canned in a heavy wall steel container. Successful extrusion with an 11.6:1 reduction in area was achieved at 1065°C. The extruded rod and the CAP processed ingot from which its preform was cut are shown in Figure 3. The conditions under which CAP processed NITINOL rod and tube can be extruded bare will require further investigation.

Final densification of preforms can be by hot extrusion. This is expected to have a significant effect on production economies projected for the straightline coupling and reducer parts, and little effect on other shapes. These latter shaped fittings would require that their ports be hot and/or cold worked by swaging to size before machining to finished dimensions. Final densification of these parts can be done directly, without canning, by hot isostatic pressing or by isostatic pressing of the heated as CAP'd preform parts contained in a crucible in a cold wall pressure chamber.<sup>15</sup>

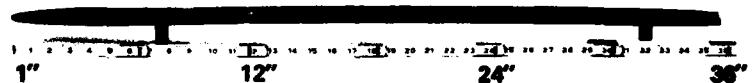
The economics of densification of CAP'd preforms of various shapes are attractive in that batches of near net shape preforms can be densified in the same way as is now done commercially for batches of castings. No canning of the parts is required, and the HIP furnace may be loaded to capacity, resulting in low per piece cost. This process is an attractive method to completely densify parts which are not to be subsequently hot worked.



**FIGURE 2. NITINOL BULK METAL PRODUCED FROM POWDER BY THE CAP PROCESS**  
(A) ROUND BAR, AS CAP PROCESSED, 92.4% OF THEORETICAL DENSITY  
(B) ROD, 98% DENSE, FOLLOWING HOT SWAGING  
(C) WIRE DRAWN FROM SWAGED ROD



EXTRUDED ROD



(B)

FIGURE 3. CAP PROCESSED NITINOL AND EXTRUDED ROD

(A) CAP PROCESSED NITINOL INGOT, 8 cm DIAMETER x 14 cm LENGTH,  
4.17 Kg (9.2 lbs).

(B) A 7.5 cm LENGTH OF THE INGOT WAS USED TO PRODUCE THE EXTRUSION,  
2.2 cm DIAMETER x 80.5 cm LENGTH.

CHAPTER 3  
SHAPE PARTS PRODUCTION

Producing preforms of several different shapes, e.g., couplings, tees, and elbows, by the CAP process would establish the feasibility of production of the broader range of pipe fitting shapes now in commercial usage. Other fittings, for example, which appear in piping systems include reducers, crosses, half ells, caps, plugs, valves, flanges, and unions.

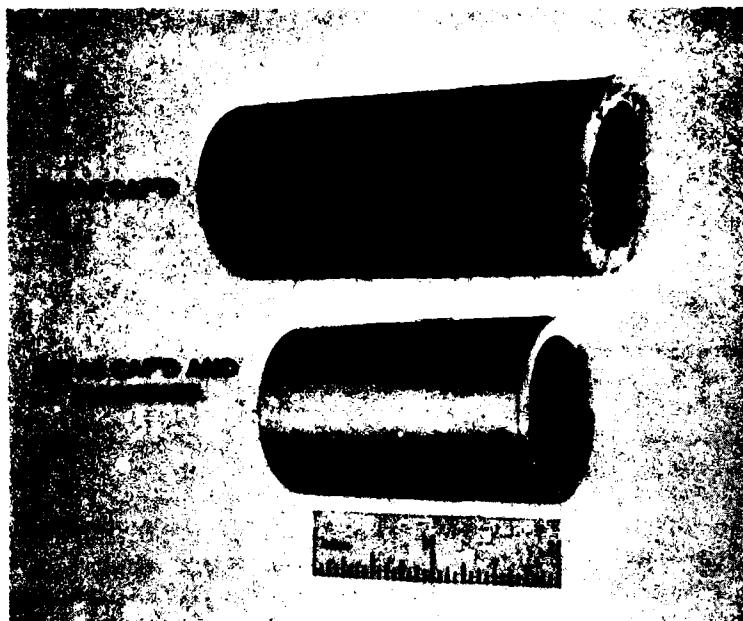
The nature of the CAP process is such that a variety of shapes and sizes can be sintered simultaneously. The different sized tubes shown in Figure 4A-D were produced singly using the CAP procedure as previously described. They could have been produced simultaneously in a single crucible. The powder used for each preform was Heat 81510 in -100 mesh size.

The costs of producing shaped parts can be allocated as follows: cost of the elemental metals in the alloy; producing the alloy; atomizing; glass mold preparation; loading, evacuating, and sintering the molds; secondary processing; and final machining. All of these operations, except mold preparation, have been performed on a commercial basis for other metals and are subject to established competitive forces. Mold making in glass for metal castings is a new process for which little guidance exists as to ultimate cost per part. Large-scale production of shapes will require fixturing of the glass lathes and the automation of the hand operations currently used to produce shapes.

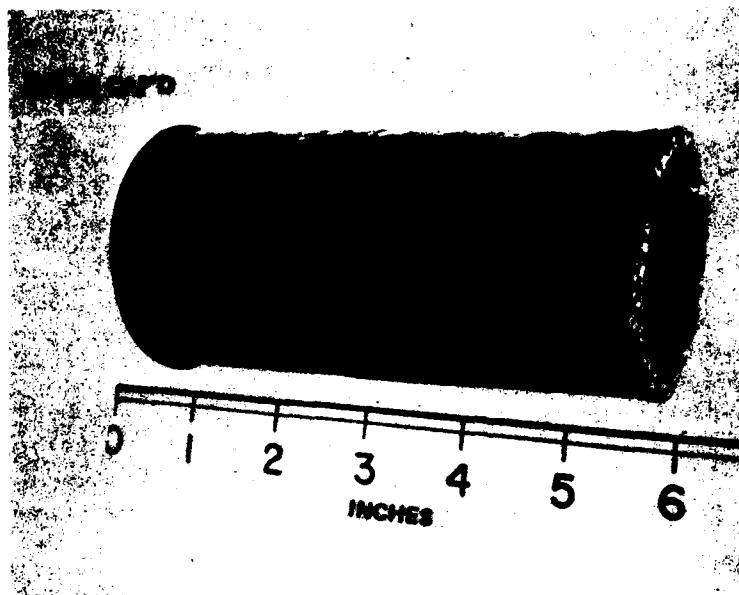
It is noted that a double wall glass tubular shape such as is used for a coupling preform can be made in production for a few dollars. This is manifest by the under \$10 price at retail for evacuated and assembled domestic Thermos® bottles. Double wall glass shapes made in more limited production, such as laboratory vacuum traps, list for \$25 each. Such a shape could produce a 2-pound NITINOL tube sufficient to make five or six couplings (a \$4 or \$5 contribution to the manufacturing cost).

The more complex glass shapes used to produce an ell or tee shape fitting are shown in Figure 5, as well as a tee produced from this style of double wall glass mold.

Figure 6A shows a drawing of double wall glass tube mold, and Figure 6B shows a tee, also in the Dewar style. Figure 6C shows a solid graphite rod substituted for the inner tube of the double wall tube design in Figure 6B. This concept offers several advantages in that it is simpler in principle than double wall tubes; it provides a smooth, dimensionally controlled inner wall after CAP processing; the graphite rod provides good heat flow into the mold interior during sintering; it is simple and easy to drill out after sintering; and it enables shapes with variable dimension internal cavities such as occur in valve bodies. Graphite cores are uniquely adapted to the CAP processing of



Nitinol tubular preform, originally 2.2 x 3.3 x 12.7 cm, 0.39 Kg (0.875 lb). Shown is a section of the preform in the "as CAP processed" condition after sandblast (A) and a machined section cut from it (B).



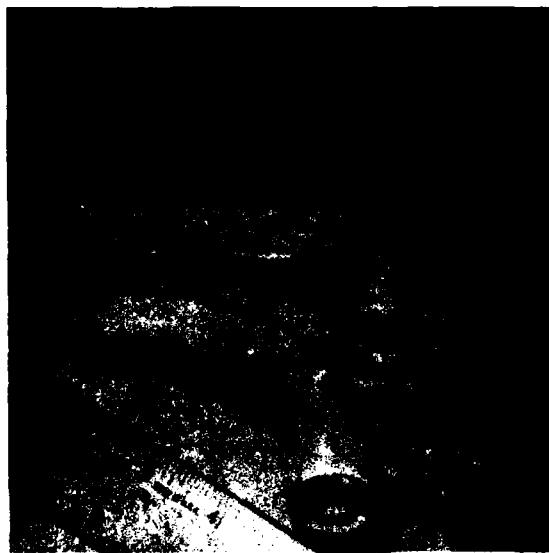
Nitinol tubular preform, 5 x 6 x 12.7 cm, 0.76 Kg (1.68 lb). This is a thin wall (10:1 diameter to wall thickness). Tubular preform is shown in the "as CAP processed" condition.

FIGURE 4. CAP PROCESSED NITINOL TUBULAR PREFORMS



Nitinol tubular preform  $6.8 \times 2.8 \times 20.6$  cm, 3.93 Kg (8.67 lbs).  
This is a heavy wall (3:1 diameter to wall thickness).  
(D) Tubular preform in the "as CAP processed" condition.  
(E) Machined sections as prepared for subsequent extrusion.

FIGURE 4. (CONTINUED) CAP PROCESSED NITINOL TUBULAR PREFORMS



BEFORE CAP PROCESSING

(A) Glass molds filled with pre-alloyed NITINOL power ready for CAP processing



AFTER CAP PROCESSING

(B) NITINOL tee preform, after CAP processing, from glass mold shown in (A)

FIGURE 5. MOLDS FOR SHAPED-FITTINGS AND CAP PROCESSING NITINOL TEE

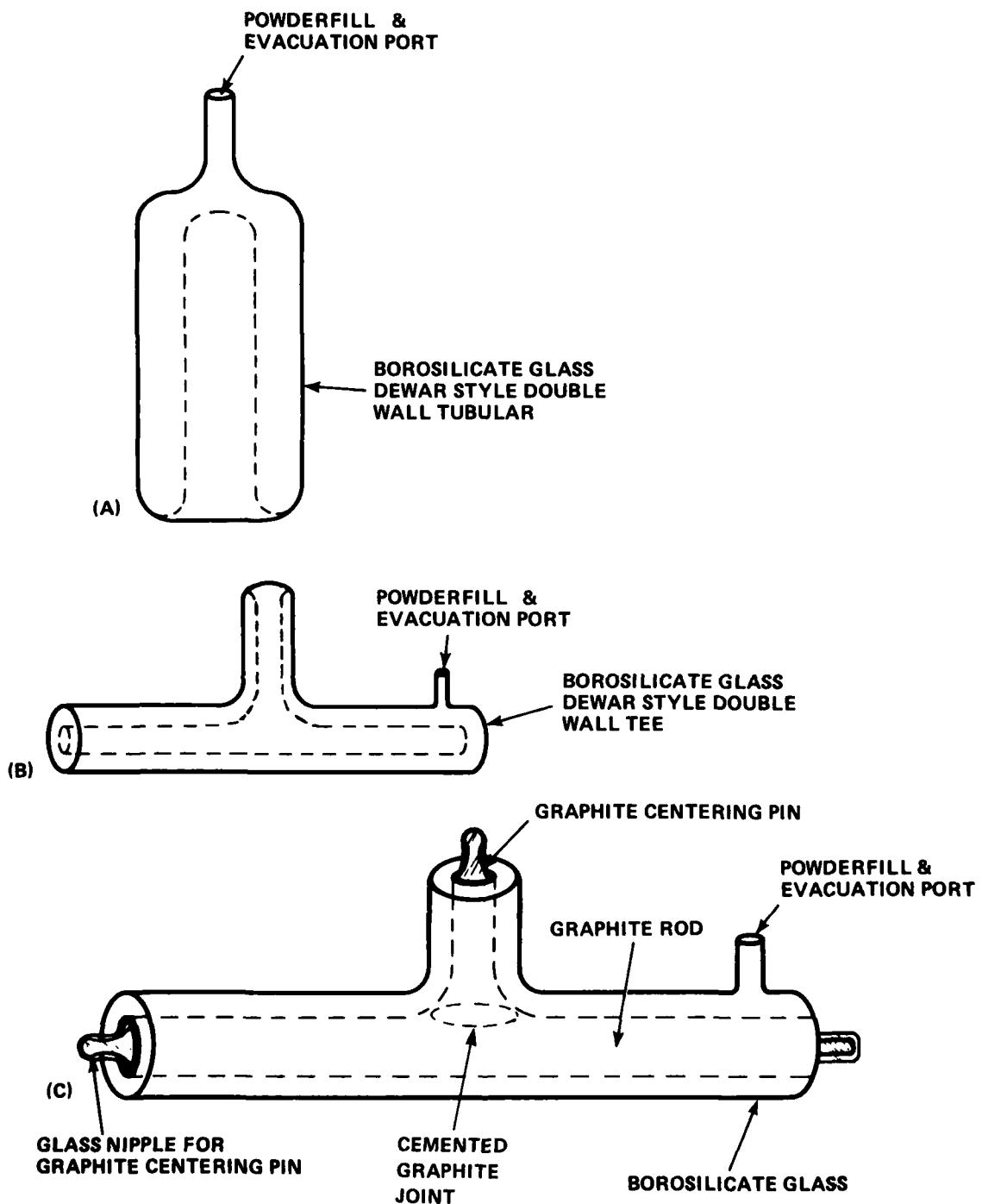
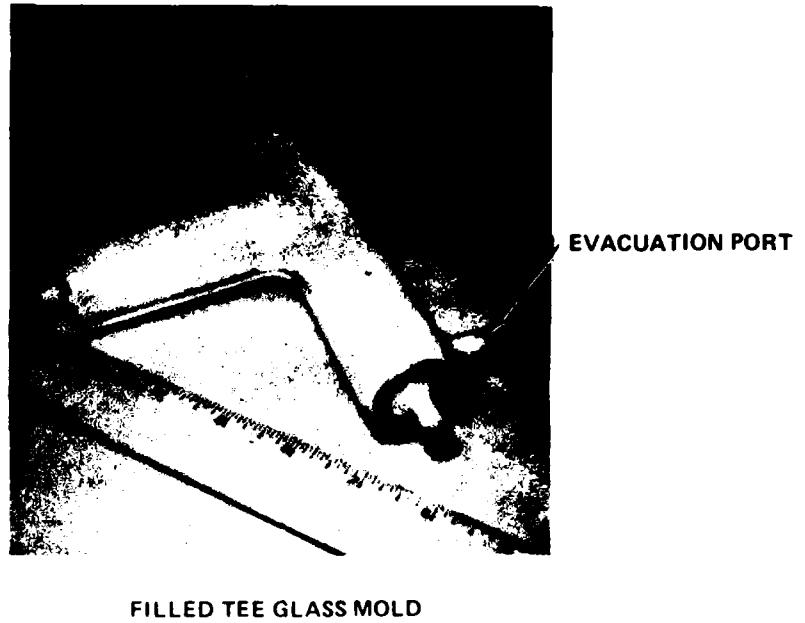


FIGURE 6. MOLD DESIGNS FOR HOLLOW SHAPES

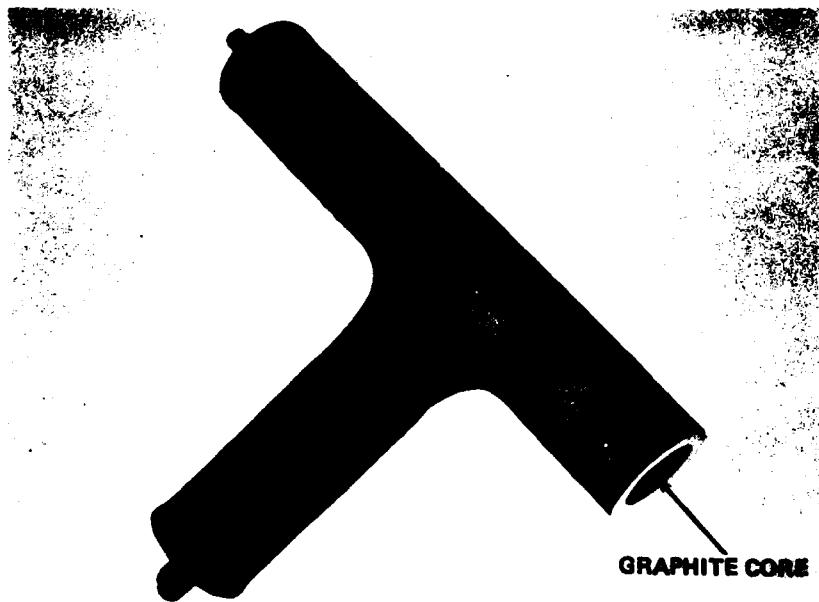
- (A) DEWAR STYLE TUBULAR
- (B) DOUBLE WALL TEE
- (C) GRAPHITE CORE TEE

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NITINOL, since no reaction between graphite and NITINOL occurs at the sintering temperatures used. A tee mold and the as CAP'd tee, following the design shown in Figure 6C, are shown in Figure 7.



FILLED TEE GLASS MOLD



AS CAP'D NITINOL TEE

**FIGURE 7. GRAPHITE-CORE TEE MOLD AND AS CAP'D NITINOL TEE. END OF THE TEE "CROSS BAR" HAS BEEN CUT OFF TO EXPOSE GRAPHITE CORE. NOTE THAT THE CORE WILL PRODUCE A UNIFORM INNER DIAMETER WHEN DRILLED OUT. GRAPHITE IS READILY MACHINABLE.**

CHAPTER 4

CONCLUSIONS

The following conclusions were derived from this study:

1. NITINOL alloy shaped products can be successfully made by the Consolidation by Atmospheric Pressure (CAP) process. This study emphasized rod, and hollow shapes such as are found in piping systems. It is concluded from the success in producing these shapes that other useful solid and hollow shapes could also be produced by the CAP process. Such near net shape parts previously considered not feasible by casting could include low noise propeller blades, cryogenic service devices, non-magnetic tools, and compromise-resistant carbide/NITINOL composite components for locks. In general the utility of the CAP process, when combined with graphite inserts, enables manufacture of shapes previously precluded due to the difficulty of casting them.
2. Hollow tubes and tees were successfully made. The solid rod produced was shown to be of good quality and was subsequently extruded, swaged, and drawn.
3. An essential parameter for part production is the use of -100 mesh pre-alloyed powder. CAP processing should be at 1175°C for a minimum of 4 hours. This yielded a minimum of 91.5 percent of theoretical density (TD). Further densification can be achieved by other methods, e.g., hot isostatic pressing, extrusion, swaging, or hot rolling as dictated by the part shape.
4. Thin wall and thick wall tabular preforms of a wide range of diameters can be made by the CAP process.
5. The nature of the process enables short turnaround time for the production of finished parts after the atomized powders are produced and are "shelf items."

CHAPTER 5  
RECOMMENDATIONS

The proof of process and manufacture of prototype shaped parts has been completed. It is recommended that the development program be extended as a manufacturing technology program.

Among the topics which should be addressed under a scaled up and more advanced technology development of the CAP process are the following:

- alloy selection via powder blending
- optimized shape memory response
- determination of mechanical properties
- optimized extrusion parameters
- economics of various production techniques, before, during, and after CAP processing
- installation techniques of multi-port pipe fittings and pressure tests of assemblies of fittings and piping.

REFERENCES

1. Evaluation of NITINOL Fittings for Joining Titanium Piping for Shipboard Applications, Lockheed Missiles & Space Company, Inc. Report, LMSC-D350045, Apr 1973.
2. Wren, R. F., and Jones R. W., Nickel-Titanium Pipe Couplings for Submarine Piping Systems, General Dynamics Task 5.41-1, Jun 1975, Contract No. 0024-75-C-2026 (Limited Distribution).
3. Keible, Edward A., Jr., "Cryofit Pipe and Tubing Joining System," in Proceedings of the Sixth Submarine Hydraulics Conference, 13 Nov 1975, Washington, DC.
4. Caskey, Maurice, R., and Embry, Gerald D., "Use of Heat Recoverable Coupling Technology in Shipyard Production," Naval Engineers Journal, Apr 1979, pp. 45 to 59.
5. Liberator, Donald J., Baskerville, James E., "The Introduction of Heat Recoverable Couplings to Ship Repair and Maintenance," Shipbuilding and Repair Symposium, American Society of Naval Engineers, 17-18 Sep 1981.
6. NAVSEA ltr 07PM2/DS Ser 20 of 25 Mar 1982 to SEA 07 (Limited Distribution).
7. Eckelmeyer, K. H., The Effect of Alloying on the Shape Memory Phenomenon in Nitinol, Sandia Laboratories, SAND 74-0418, Mar 1975.
8. Van Cleave, David A., "Cold Pressing Opens the Door on Complex Shapes," Iron Age, Vol. 219, No. 18, 9 May 1977, pp. 39 to 41.
9. Chandler, Harry E., "New Directions for Nonferrous Metals," Metal Progress, Vol. 125, No. 7, Jun 1984, p. 29.
10. Goldstein, David M., and McNamara, Leo J., Proceedings of the NITINOL Heat Engine Conference, NSWC MP 79-441, 27 Sep 1978.
11. "Manufacturing Technology Ships Overhaul Investment Opportunity Study," Navy Manufacturing Technology Bulletin, No. 83, Sep 1980.
12. Baskerville, James E., Whiddon, W. David, "Ship Design--Performance Through Innovation," Naval Engineers Journal, Feb 1981, pp. 33 to 44.

REFERENCES (Cont.)

13. NAVSEA ltr 90M/RR Ser 168 of 9 Nov 1981 to CNM.
14. Black, Herbert L., Somerville, Mark, Schwertz, Jerome, "Powder Metallurgy," U.S. Patent No. 4,227,927, 14 Oct 1980.
15. Goldstein, David M., "Method of Compacting Powders," U.S. Patent Application, Navy Case #66879.

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